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Sustainable and efficient cork - inorganic polymer composites: An innovative and eco-friendly approach to produce ultra-lightweight and low thermal conductivity materials

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ABSTRACT

In this investigation cork was used as a low density aggregate in the production of ultra-lightweight and low thermal conductivity inorganic polymer (geopolymer) composites. This novel and highly sustainable material, synthesised at room temperature (23 °C), may decrease the energy losses inside buildings, thus contributing to the United Nations development goals regarding energy and climate change. The ultra-low density (260 kg/m^3) and low thermal conductivity (72 mW/m K) shown by the cork-composites are the second lowest ever reported for inorganic polymer composites, only being surpassed by that of polystyrene-inorganic polymer composites. However, cork is a fully renewable and sustainable resource, while polystyrene is manufactured from non-renewable fossil fuels, and for that reason our strategy has an additional sustainability advantage. Moreover, the cork-inorganic polymer composites do not release any toxic fume when under fire conditions, which is a major advantage over polymeric-based foams.

1. Introduction

The building industry faces tremendous challenges to cope with the sustainable development goals set by the United Nations regarding energy, climate change and depletion of natural resources. Buildings are responsible for circa 40% of the energy consumption, and 36% of the CO_2 emissions, in the EU [1]. Increasing the energy efficiency of buildings is, therefore, mandatory to achieve higher sustainability levels in this sector. One stimulating approach to decrease buildings' energy consumption is the development of lightweight and low thermal conductivity materials, which may decrease the energy losses inside buildings.

Inorganic polymers (geopolymers) have emerged in the past few years as an excellent alternative to the use of Portland cement, due to their much lower environmental footprint in terms of raw materials [2] and embodied CO_2 [3]. This innovative binder also presents other interesting properties, such as greater chemical resistance [4] and thermal durability [5]. Nevertheless, concerns regarding the inorganic polymer production cost and actual CO_2 emissions have delayed this technology widespread. To fully explore the inorganic polymer environmental benefit in comparison with ordinary Portland cement the mixture design (e.g. raw materials and activators nature and content) should be carefully considered. This topic is addressed in detail in Refs. [6,7].

Inorganic polymer foams combine the properties of the inorganic polymer technology with those of lightweight materials (e.g. low density and thermal conductivity), and may be an exciting approach to decrease the energy losses inside buildings. These foams are usually prepared using foaming agents (e.g. metallic aluminium [8]; hydrogen peroxide [9]) or by adding lightweight aggregates (e.g. expanded polystyrene [10]; rubber [11]). The precise control of the inorganic polymer foams properties, namely the pore size distribution, is challenging, and therefore the use of lightweight aggregates is particularly interesting. Various artificial lightweight aggregates have been studied, such as those produced form rice husk [12], fly ash and mine tailings [13], among others [14]. Despite their interesting results, the use of a natural, sustainable, low cost and lightweight aggregate, instead of synthetic or non-renewable aggregates, would be both economic and environmental beneficial for the construction sector. In this study, an innovative and environmentally friendlier strategy – using expanded

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cork granules, coming from corks' agglomeration industry, as lightweight aggregate – was implemented. Cork is an extraordinary renewable resource, extracted from an oak tree (*Quercus suber* L.) without damaging the tree. Worldwide cork production is estimated to reach 201 ktons/year, and Portugal is the world's largest producer accounting for ~50% of corks' production [15]. This unique and highly sustainable material presents outstanding properties (e.g. thermal and acoustic insulation; high porosity) making it suitable for a wide array of applications, ranging from construction [16] and wine products to precursors of activated carbons [17] or ecoceramics [18]. Cork has a highly porous microstructure, consisting of hollow polyhedral cells, with a hexagonal honeycomb shape (radial direction) and rectangular shape (transverse side or top directions). Cork properties are described in detail in Refs. [19,20]. One other remarkable feature of cork is its very low density (as low as 120 kg/m^3) [19], which endows its use as a light aggregate in mortar [21] or concrete [22] production, replacing mineral aggregates. Besides its lower density, the use of cork has several more advantages over other lightweight aggregates, in particular its low water permeability and thermal conductivity, and excellent sound absorption, fire resistance and durability. These properties suggest the feasibility of using cork as a light aggregate in the production of low thermal conductivity inorganic polymer composites. However, and to the best of our knowledge, this strategy has never been reported up to now. Additionally, there is little literature on the use of cork to produce inorganic polymer composites, the exceptions being the work of Roper et al. [23] which used cork as a reinforcement agent to produce sodium inorganic polymer composites, and that of Sugagar et al. [24] which added cork to metakaolin-zeolite inorganic polymer which were then used to remove heavy metals from synthetic wastewaters. Roper et al. [23] added between 15 wt.% to 60 wt.% of cork (~2 mm) to the compositions and evaluated the composites mechanical performance, an increase in the flexural strength being observed when increasing the cork amount in the compositions. Sugagar et al. [24] added 20 wt.% cork residue as a filler to the metakaolin-zeolite inorganic polymer and then after curing, the specimens were crushed and the corresponding powders were used as adsorbent material. This investigation will evaluate for the first time the possibility of producing ultra-lightweight cork-based inorganic polymer composites exhibiting low thermal conductivity, which are envisioned for non-structural applications. The influence of cork incorporation content on the inorganic polymer composites' mechanical (flexural and compression), thermal (conductivity and stability) and physical properties (apparent density) was evaluated.

In addition to their ultra-low density, the cork-inorganic polymer composites are a safer and environmentally friendlier alternative to the use of polymeric-based thermal insulating foams (e.g. polyurethane or polystyrene, usually made from fossil fuels) since cork is a 100% renewable material, and under fire conditions does not release toxic fumes.

Cork is an organic and biodegradable material, nevertheless, the durability of cork is substantially superior to that required for construction materials. In fact, it has been demonstrated that cork products remain virtually unchanged for more than 50 years [25]. Nonetheless, future work will address the durability of the produced cork-inorganic polymer composites.

2. Experimental conditions

2.1. Materials

Expanded black cork blocks are widely used as thermal insulating building materials, being the only insulation material in the market with a negative carbon footprint (−116.229 kg CO_2 equivalent per m^3) [26]. During its production by the agglomeration industry, around 15% of rejected cork slabs are produced, and then sent to a second trituration [27]. In this work, the co-product from this second trituration was used due to its low economic value. These black expanded cork granules (apparent density 70 kg/m^3) were used *as-received* as light aggregates in the production of cork-inorganic polymer composites. This type of cork is produced from low grade cork [26] that cannot be used in other applications (e.g. wine stoppers). These granules are placed in an autoclave at high temperatures (300 °C) and pressures [19] without using additives. This industrial process promotes microstructural and compositional changes on the cork, leading to the granules' expansion.

Metakaolin (Argical™ M1200S, Univar) was selected as the geopolymerisation precursor, since it is the benchmark aluminosilicate [28]. Nevertheless, future work will evaluate the possibility of using industrial wastes, instead of metakaolin, to further decrease the inorganic polymer production cost and carbon footprint. This possibility was been demonstrated by the authors by using various waste streams [29,30].

Chemical activation was performed using a mixture of 10 M sodium hydroxide solution (ACS reagent, 97%; Sigma Aldrich) and sodium silicate solutions (SiO_2/Na_2O = 3.1; H_2O = 62.1 wt.%; Quimialmel; Portugal).

2.2. Cork-inorganic polymer composites

Considering previous works by the authors [28,30], and preliminary tests that assessed the influence of cork on the slurries' workability, a reference composition (prepared without cork) was established (see Table 1). Then, six different amounts of expanded cork granules, ranging from 5 wt.% to 30 wt.% (corresponding to 65 vol.% to 92 vol.%) were added to this. These amounts were selected considering the ultimate goal of this study (development of ultra-light inorganic polymer composites), but also since this natural aggregate is the less expensive component in the produced composites. In this context, the amount of cork in the composites was maximized reaching 92 vol.%. Higher amounts were not evaluated due to strong decrease on the slurries' workability.

The procedure used for the inorganic polymer synthesis has been described in detail in Refs. [29,31]. Cork was added (amount depending on the composition) to the prepared inorganic polymer slurry, and then mechanically mixed for 1 min. The mixture was then poured into steel moulds, which were covered with a plastic film to limit the moisture loss. All the samples were cured at ambient conditions (23 °C; 65% relative humidity) to increase the global sustainability of the process. After 24 h, the specimens were demoulded and then cured at the same conditions until their mechanical and thermal characterisation.

2.3. Materials characterisation

2.3.1. Microstructure tests

The microstructure of the cork granules and the cork-inorganic polymer composites was studied by scanning electron microscopy (SEM – Hitachi SU 70 equipped with energy dispersion spectroscopy – EDS Bruker).

To evaluate the cork granules size image analysis was used. The images were acquired with a digital camera coupled to an optical

Table 1
Mixture composition of the cork-inorganic polymer composites.

Sample ID	Mixture proportion (wt.%)			Cork	
	MK	Sodium silicate	NaOH	(wt.%)	(vol.%)
Reference	37	45	18	–	–
F1				5	65
F2				10	79
F3				15	85
F4				20	88
F5				25	90
F6				30	92

microscope (Leica EZ4HD), and then the software ImageJ was used to determine the particles size.

2.3.2. Mechanical tests

The mechanical performance of the composites was evaluated by performing flexural and compression tests on samples (4 cm × 4 cm x 16 cm) after 28 curing days, following the standard EN 1015-11:1999 [32], using a Universal Testing Machine (Shimadzu, model AG-25 TA), running at a displacement rate of 0.5 mm/min, was used. Three replications were used to calculate the mean values.

2.3.3. Physical tests

The specimens' bulk density (calculated by measuring the samples weight and volume) and thermal conductivity were evaluated at the 28th day on cubic samples (4 cm × 4 cm x 4 cm). Three specimens per composition were measured, and the arithmetic mean value presented.

2.3.4. Thermal tests

To evaluate the influence of the cork on the temperature fluctuation when submitted to a temperature gradient, a simple, but effective, validation test was performed on two samples: the matrix and the highest cork-containing composite. In this test, a cubic specimen (4 cm × 4 cm x 4 cm) was mounted in a sample holder (thermal insulating extruded polystyrene - XPS), which was then connected to a climatic chamber. In this way, the internal surface (called the *hot surface*) of the sample was in contact with a high and constant temperature, imposed inside the climatic chamber (80 °C; 65% relative humidity), while the external samples surface (called the *cold surface*) was at a lower temperature (room temperature = 25 ± 2 °C). For temperature monitoring, thermocouples were placed at the internal (*hot surface*) and exterior (*cold surface*) surfaces, and then connected to a data acquisition device (Data Logger Switch Unit 34970A; Agilent). Two additional thermocouples were used to control the temperature inside and outside the climatic chamber (Fito-clima 300 EP10; Aralab). After placing the sample in the holder, the temperature fluctuation was measured over two hours.

Thermal conductivity measurements were performed using a heat flow meter apparatus according to standard ASTM C518-04 [33]. In this test the sample is placed between two parallel plates and then a heat flux is established trough the specimens by two heat flux transducers.

Thermogravimetric analysis were performed using a Labsys TG-DSC16 (Setaram), heating the samples at 5 °C/min under air.

To further evaluate the specimens' thermal stability, the samples (4 cm × 4 cm x 1 cm) were fired at different temperatures, ranging from 200 °C to 600 °C, according to the following cycle: i) 5 °C/min up to the maximum temperature; ii) 120 min dwell time at this temperature; iii) cooling at 5 °C/min to room temperature.

3. Results and discussion

3.1. Cork characterisation

Fig. 1a presents a photograph of the black expanded cork granules used here as lightweight aggregate. The average size of the granules, determined using image analysis software (ImageJ), is 5.7 ± 1.1 mm (Fig. 1b). The granules show characteristic hexagonal cells (see SEM image in Fig. 1c) similar to that of untreated cork (a detailed microstructural and thermal analysis of untreated cork can be found in Ref. [34]), but unsurprisingly, the diameter of the hexagonal cells in these granules (~25–50 μm) and the prism base edge (~20–32 μm) is higher than those typically reported for untreated cork (~15 μm [35] and 13–15 μm [36], respectively), a consequence of the industrial thermal treatment (see details in section 2.1). The EDS map of the cork granules (see Fig. 1d) shows that carbon is the dominant element in the corks composition. Nevertheless, a small amount of aluminium (below 0.5 wt. %) was also detected.

3.2. Cork-inorganic polymer composites characterisation

3.2.1. Microstructural analysis and composite apparent density

Fig. 2a shows representative photographs of the various cork-inorganic polymer composites, illustrating a homogeneous distribution of the cork granules in the inorganic polymer matrix. This is extremely relevant and demonstrates that no segregation took place in the studied composites, which was attributed to the optimised viscosity of the slurry. Indeed, aggregates segregation is known to negatively affect the composites strength and durability [37].

The apparent density of the cork granules is significantly lower than that of the inorganic polymer slurry. Therefore, the volume occupied by the cork granules in the composite will be substantially greater in comparison with the binder. This feature can be easily observed from the comparison between the volume of the slurry and that of the highest amount of cork used here (see Fig. 2b).

Fig. 2c presents a digital photograph of the composite containing 92 vol.% cork, this being the lightest sample. As observed, the cork granules are bonded together by the inorganic polymer matrix. SEM micrographs of this composite are presented in Fig. 3. Fig. 3a shows that the surface of the cork granules is covered by a thin inorganic polymer layer, as demonstrated by the EDS map (see inset). Despite this, the highly porous microstructure of cork is preserved, as shown in Fig. 3b. Fig. 3b also shows an excellent interface between cork and matrix, suggesting strong bonding between the aggregate and the matrix. Fig. 3c shows the fracture surface of the composite after mechanical tests, while the EDS elemental mapping is given in Fig. 3c_1-c_3. As observed, the left-side of the micrograph shows an inorganic polymer gel resulting from the alkaline activation of metakaolin which is composed by homogeneously distributed Al and Si, while the right-side of the SEM micrograph shows the cork aggregate mostly composed by C, as expected.

To better characterise the interface between the matrix and the aggregates EDS line profile analysis using SEM was performed. Fig. 4 presents the SEM/EDS line profile for the composition containing 65 wt. % cork. The SEM micrograph does not show the presence of a porous interfacial transition zone (ITZ). In fact, there isn't any clear gradual transition between the dense matrix and the porous aggregate (cork). This remark is corroborated by the EDS line profile showing a fairly stable Si and Al profile in the matrix (minor differences are attributed to topography), and then a sudden change in the composition, and therefore in the Si, Al and C profile, at the vicinity of the interface. This behaviour was also observed for the other cork-inorganic polymer composites (not shown here for the sake of brevity). These results differ from those of reported by Singh et al. [38] for fly ash-slag inorganic polymer concrete in which a ITZ comprised of inorganic polymer gel, voids, unreacted particles and cracks was observed. Similar to our observations, Yliniemi et al. [13] did not observe a visible porous ITZ, however, they did observe some gaps (tens of microns wide) between the fly ash geopolymer aggregates and the matrix, which was attributed to the aggregates shrinkage.

The influence of cork incorporation content on the composites' apparent density is illustrated in Fig. 5. The density of the reference composition (prepared without cork) was 1.15 g/cm^3, while those of the cork-containing composites varied between 0.83 g/cm^3 and 0.26 g/cm^3. To better illustrate the density change when the cork content increases, the density drop was included in Fig. 5. The composite containing the highest amount of cork exhibited 77% lower density than the matrix. The latter is attributed to the substantially lower density of cork in comparison with that of the inorganic polymer matrix. These results are in line with the work of Panesar and Shindman [22] which observed a decrease in the mortars' density with increasing percentage of cork.

The lowest apparent density achieved (260 kg/m^3) was compared with other literature studies addressing the synthesis of lightweight inorganic polymer composites or inorganic polymer foams (prepared

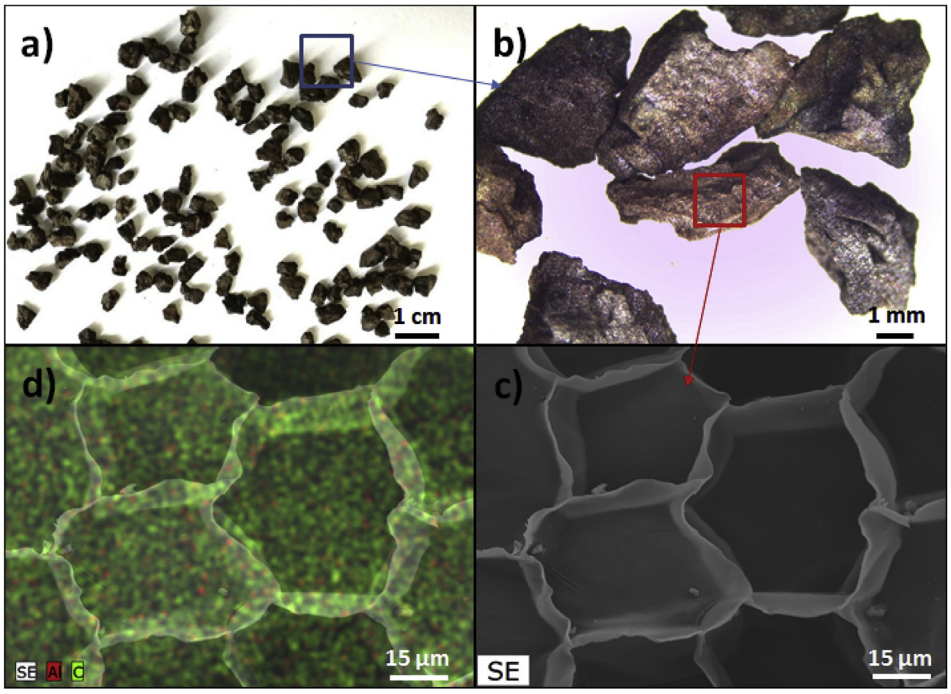

Fig. 1. (a) Digital photograph of the black expanded cork granules, b) optical and c) SEM micrographs illustrating the corks' morphology and microstructure, and d) EDS elemental mapping of the granules.

using foaming agents), and results are shown in Fig. 6.

As observed, the cork-inorganic polymer composites are amongst the lightest ever reported for inorganic polymer composites, their apparent density being 7.4 times lower than that reported for expanded vermiculite alkali activated composite (1918 kg/m^3) [39]; between 4.1 and 3.1 times lower than a crumb rubber-inorganic polymer composite (1067 kg/m^3) [11], cellular alkali-activated fly ash concrete (940 kg/m^3) [40] and expanded glass-inorganic polymer composite (800 kg/m^3) [41]; and two times lower than expanded polystyrene (EPS)-inorganic polymer composites (516 kg/m^3) [10]. In fact, the density of the cork-inorganic polymer composite is only surpassed by that reported by Duan et al. (100 kg/m^3) [42]. However, in their study polystyrene particles were used as a lightweight aggregate and hydrogen peroxide as foaming agent, while here a sustainable, completely renewable aggregate presenting a much lower carbon footprint than the polymeric particles was used, and without any foaming agent. Hence, in the present study a much more eco-friendly strategy was used. These are very promising results, suggesting that the cork-inorganic polymer composite can be an exciting way to decrease the weight of building materials, and as a consequence their transportation costs.

Furthermore, the values achieved here also lower than those reported for several inorganic polymer foams prepared using hydrogen peroxide [9,43,44], metallic powders [8,45], commercial surfactants [46] or by an air entraining agent [47]. They are similar to those reported by Feng et al. by using hydrogen peroxide as foaming agent [48], which further demonstrates the potential of this innovative composite to be used as a building material for non-structural applications (e.g. partition board and wall panels).

3.2.2. Flexural and compressive strength measurements

The flexural and compressive strength of the matrix and the various composites is presented in Fig. 7. After 28 days, the flexural and compressive strength of the inorganic polymer matrix reaches 2.35 MPa and 14.00 MPa (see inset), respectively. The incorporation of cork induces a strong decrease in both the flexural and compressive strength, the former ranging from 1.55 MPa to 0.29 MPa, and the latter from 2.86 MPa to 0.23 MPa. This behaviour is in line with previous investigations which showed a decrease in the mechanical performance of cement-based mortars when increasing the amount of cork [22,49]. Borges et al. [49] reported a major decline in the flexural (between 72 and 75%) and the compressive (between 84 and 97%) strength for the cement-based mortars in which expanded cork granules were used in comparison with the sand mortar. Likewise, the cement-cork composites prepared by Brás et al. [50] and containing 80% of cork, instead of sand, showed a reduction boty in the compressive (~80%) and the flexural (~65%) strength in comparison with the reference mortar.

The pronounced drop in mechanical strength, particularly compressive, observed for the cork-containing inorganic polymer composites is attributed to the very high volume of cork used in the compositions, ranging from 65 vol.% to 92 vol.%. Despite this, the lowest values attained here for the compressive strength (0.23 MPa) are still greatly superior to those of many other lower thermal conductivity materials, such as foamed concrete containing expanded polystyrene particles (0.08 MPa; 82.2 vol.% EPS) [51], aerogel-containing mortar (< 0.1 MPa; 80 vol.% aerogel) [52], straw-plaster composite (0.004–0.071 MPa) [53]. The values reported here are similar to other studies addressing the synthesis of inorganic polymer foams prepared with blowing agents (0.26 MPa) [9] or through saponification reactions (0.2–0.4 MPa) [54], perlite-based inorganic polymer foams (0.250–0.780 MPa) [55], and to other thermal insulating building materials (e.g. foamed glass and wood fibre board) [56].

Characteristic stress-strain curves (compression tests) for the inorganic polymer and the various cork-containing composites are shown in Fig. 8. The abovementioned lower mechanical resistance of the composites is clearly depicted from the curves. Despite this, all composites showed a graceful fracture, while a brittle fracture was observed for the matrix. This behaviour can be attributed to the high compressibility of cork [57], that can reach strain up to 70% [58]. After the initial elastic bending (up to strains of ~5%) of the cork cell walls, a large plateau with a small slope is observed due to the progressive buckling of the cork cells walls [59]. This feature is clearly demonstrated by the significant increase in the composites' maximum strain, reaching ~30% in comparison with the non-cork-containing matrix (only ~3%).

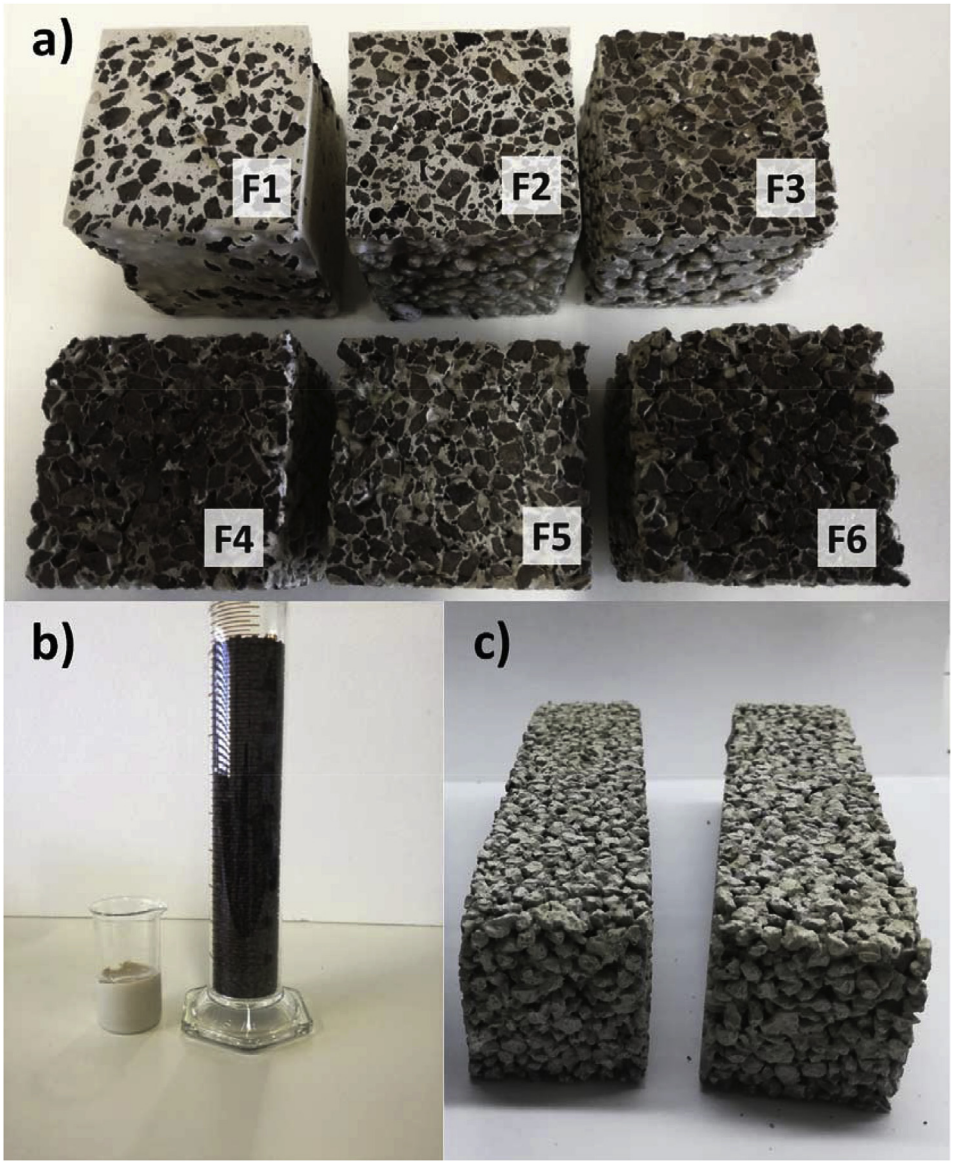

Fig. 2. (a) Digital photograph of the various cork-inorganic polymer composites, illustrating the cork's distribution in the inorganic polymer matrix, b) comparison between the volume of the inorganic polymer slurry and that of the highest amount of cork used to prepare the composites, and c) typical photograph of the composites prepared with 92 vol.% cork.

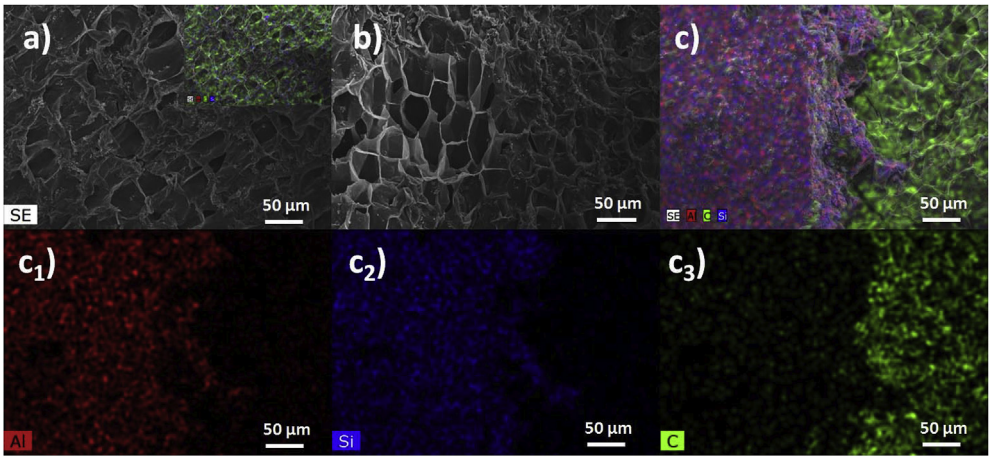

Fig. 3. (a, b) SEM micrographs of the cork-inorganic polymer composite containing 92 vol.% cork and c) EDS elemental mapping. The inset micrograph in Fig. 3a shows the presence of a thin geopolymeric layer covering the corks' surface.

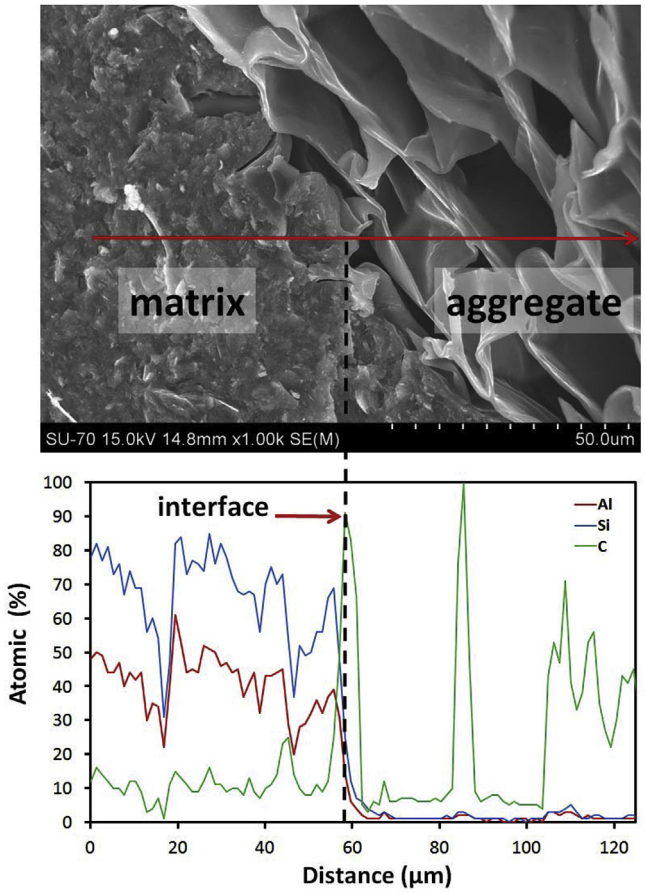

Fig. 4. SEM micrograph and EDS line profile of the cork-inorganic polymer composite containing 65 wt.% cork showing the interface between the matrix and the aggregate (cork).

3.2.3. Thermal performance

3.2.3.1. Temperature variation in samples. The results for the pure inorganic polymer matrix and the composite with the greatest quantity of cork (92 vol%) are presented in Fig. 9. The thermal performance of these two specimens is significantly different throughout the test. In the matrix, a sharp increase in the *hot surface* temperature is observed immediately after the beginning of the test, and there is a rapid increase in temperature during the first 10 min, reaching 68.6 °C at this time. Afterwards, a gentler increase in temperature is observed, up to 70.1 °C after 120 min. The *cold surface* temperature showed a much more moderate increase with time, reaching 35.8 °C after 120 min.

Not surprisingly, the cork-containing composite showed much greater thermal inertia than the matrix. In fact, with cork, the *cold surface* temperature remained mostly constant throughout the test, suggesting that the composite has much lower thermal conductivity (see section 3.2.3.2). The *hot surface* (in direct contact with an 80 ºC atmosphere) temperature increased from ~24 °C to 46 °C in the first two minutes, before stabilising at values around 37.5 °C after ~20 min, and for the remainder of the 120 min. The distinct temperature fluctuation observed for the two specimens is better illustrated by the temperature gradient (difference between the temperature of the matrix and the cork-composite) shown in Fig. 9b. As depicted, differences up to 38 °C and 25 °C in the *hot* and *cold surface* were attained, clearly demonstrating the much lower thermal conductivity of the cork-composite. This will be further discussed in the next section.

3.2.3.2. Thermal conductivity measurements. The thermal conductivity of the various cork-composites is shown in Table 2. The thermal conductivity of the matrix was not measured since the objective of the present work is the production of low thermal conductivity materials. As expected, the thermal conductivity drops from 156 mW/m K to 75 mW/m K when the volume of cork in the composites increases from 65 vol.% to 92 vol.%. Similar trend of decreasing thermal conductivity with higher cork contents was also observed for cork-concrete composites [22].

The lowest thermal conductivity here achieved for the cork-inorganic polymer composites (72 mW/m K) was compared with other literature values reported for various inorganic polymer composites and inorganic polymer foams and results are shown in Fig. 10. The thermal conductivity of these novel cork-composites is amongst the lowest ever reported for inorganic polymer composites, being 6.5 times lower than that reported for oil palm shell foamed inorganic polymer concrete [60]; roughly three times lower than alkali activated fly ash concrete [40] and crumb rubber-inorganic polymer composites [11]; and ~1.5 times lower than EPS-inorganic polymer composites [10] and expanded glass-inorganic polymer composites [41]. In fact, the low thermal conductivity of the cork composites is only beaten by that of polystyrene-inorganic polymer composites [42], but those authors used both polystyrene particles and a foaming agent, while in the work reported here only cork (a sustainable lightweight aggregate) was used.

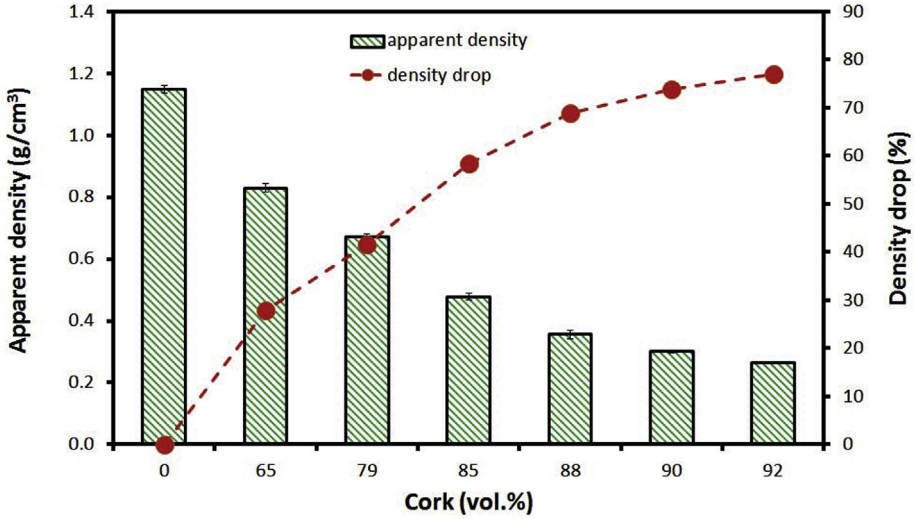

Fig. 5. Apparent density of the cork-inorganic polymer composites at the 28th day illustrating the influence of the cork amount.

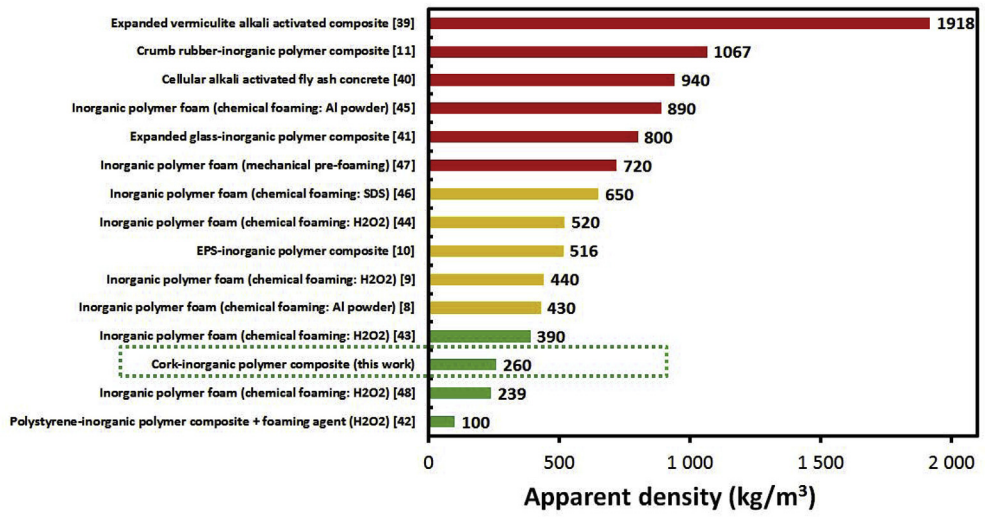

Fig. 6. Apparent density of various inorganic polymer composites and foams reported in literature. Red bars correspond to densities above 700 kg/m^3, orange bars between 700 and 400 kg/m^3 and green bars below 400 kg/m^3. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Additionally, the cork composite's thermal conductivity is also inferior to several other inorganic polymer foams (e.g. Refs. [46,47,56,61]) and to Portland cement-based mortars [62,63] and lime-based plaster [64], which further demonstrates the remarkable potential of these innovative and eco-friendly materials for low thermal conductivity applications.

In addition to their low thermal conductivity, the cork-inorganic polymer composites are also expected to show interesting acoustic insulation properties which will set them apart from other low thermal conductivity materials. Indeed, cork's acoustic insulating properties are widely acknowledged [19]. Future work will address the acoustic performance of the cork - inorganic polymer composites.

3.2.3.3. Thermal stability measurements. To evaluate the thermal stability of the composites, selected specimens were heated to various temperatures (from 200 °C to 600 °C) and kept for 2 h at that temperature. Digital photographs, taken before and after thermal treatment, are shown in Fig. 11. Inorganic polymers are known to present high temperature resistance (up to 800 °C) [65], while the thermal decomposition of cork is initiated earlier, typically at around 200 °C [66].

Heating the cork - inorganic polymer composites up to 200 °C does not induce any macroscopic change in the various specimens (see Fig. 11). However, when raising the temperature to 400 °C, several cracks are visible in the composite containing the lowest level of cork (65 vol.%). Some pores were observed in the composite containing 85 vol.% cork, while the composite containing 92 vol.% cork partially disintegrates. Increasing the temperature to 600 °C further intensifies the modifications of the composites macrostructure, this being particularly visible in the composite containing the highest levels of cork.

To better understand their thermal stability, the TG curves of the cork granules, the inorganic polymer matrix, and the highest cork-containing composite are shown in Fig. 12. The TG curve of the inorganic polymer shows that the most relevant mass loss (14.2%) occurred below 200 °C, associated with the removal of physically adsorbed water. Then, a gentler weight loss rate was observed between 200 °C and 800 °C. Between these temperatures, a weight loss of 6.2% was observed which was attributed to the dehydroxylation of the chemically bonded water. These findings are in line with previous reports performed in inorganic polymers in which dehydration and dehydroxylation of free and chemically bound water were observed below 200 °C and between 250 °C and 600 °C [67].

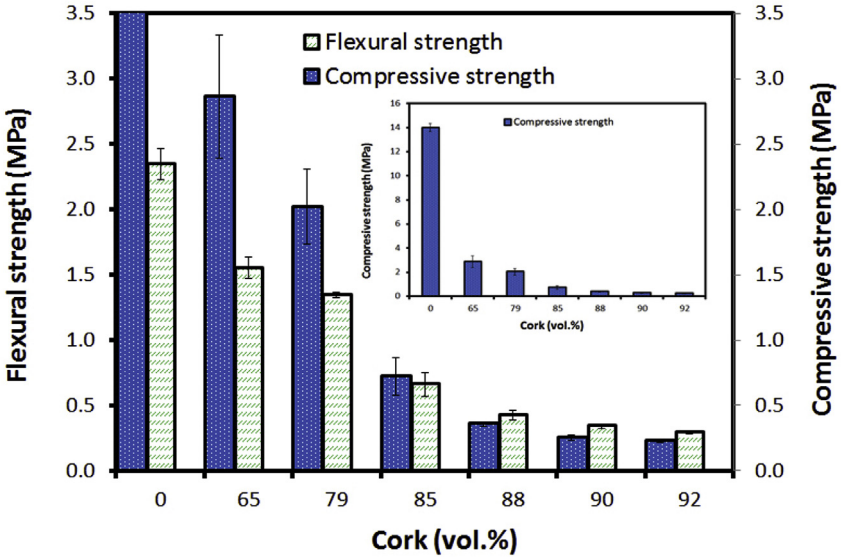

Fig. 7. Flexural and compressive strength of the cork-inorganic polymer composites prepared with various cork amounts. The inset shows the compressive strength of the matrix.

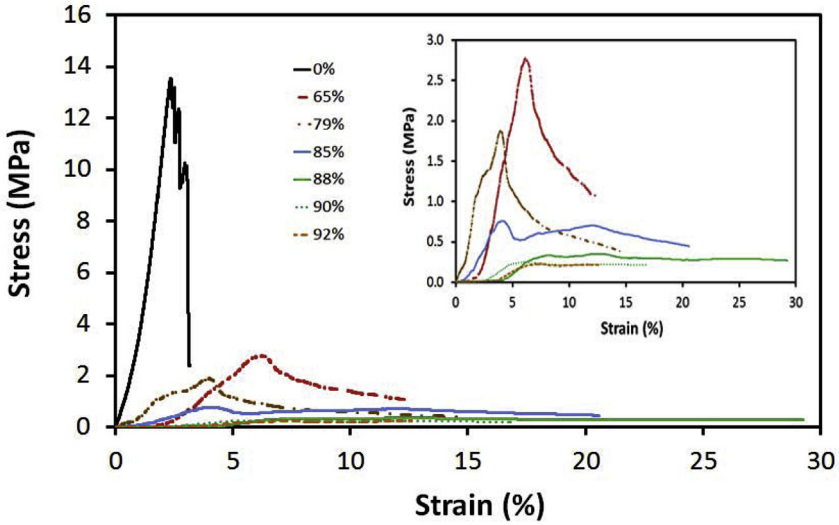

Fig. 8. Compression stress-strain curves of the various cork-inorganic polymer composites.

The expanded black cork granules are thermally stable up to 200 °C, while above this temperature and up to 600 °C a massive weight loss occurs (88.5%), due to the degradation of volatile components naturally occurring in cork. Other literature studies have also reported that the thermal decomposition of cork starts at temperatures above 200 °C, increasing with temperature and time [34,66]. This feature explains the partial disintegration of the highest cork-containing composite observed at 400 °C, and the almost complete disintegration observed at 600 °C. In line with this remark, the cork-inorganic polymer composite TG curve shows a significantly higher total weight loss in comparison with the matrix (40.3% instead of 20.4%), caused by the cork degradation. However, these results show that the cork-inorganic polymer composites are thermally stable up to 200 °C, which surpasses the maximum operating temperature of common insulating materials such as EPS and XPS, which are 80 °C and 75 °C, respectively [55]. Furthermore, under fire conditions, neither cork [19] nor the inorganic polymer matrix [68] release any toxic fumes and, therefore, neither will the composites. This is a crucial advantage over polymeric-based thermal insulating materials such as polyurethane foams, XPS and EPS, which do release toxic fumes upon combustion.

4. Conclusions

This work evaluates, for the first time, the possibility of using cork as a light aggregate in the production of inorganic polymer composites,

Table 2
Thermal conductivity for various cork-inorganic polymer composites.

Sample ID	Cork (vol.%)	Thermal conductivity (mW/m K)
F1	65	156 ± 5
F2	79	141 ± 6
F3	85	98 ± 5
F4	88	89 ± 6
F5	90	80 ± 6
F6	92	72 ± 4

envisioned for low thermal conductivity applications. Ultra-lightweight (260 kg/m^3) and low thermal conductivity cork composites (72 mW/m K) were produced using a simple and environmentally conscious approach. These values are among the lowest ever reported for inorganic polymer composites, only being surpassed by polystyrene-inorganic polymer composites. However, cork is a fully renewable and sustainable resource, while polystyrene is manufactured from non-renewable fossil fuels, and for that reason our strategy is more sustainable.

Furthermore, the cork-composites are thermally stable up to 200 °C, which surpasses the maximum operation temperature of common insulating materials, such as EPS and XPS. Moreover, the cork-composites do not release any toxic fumes when under fire conditions, which is a major advantage over polymeric-based foams.

Future work will address the acoustic performance and the

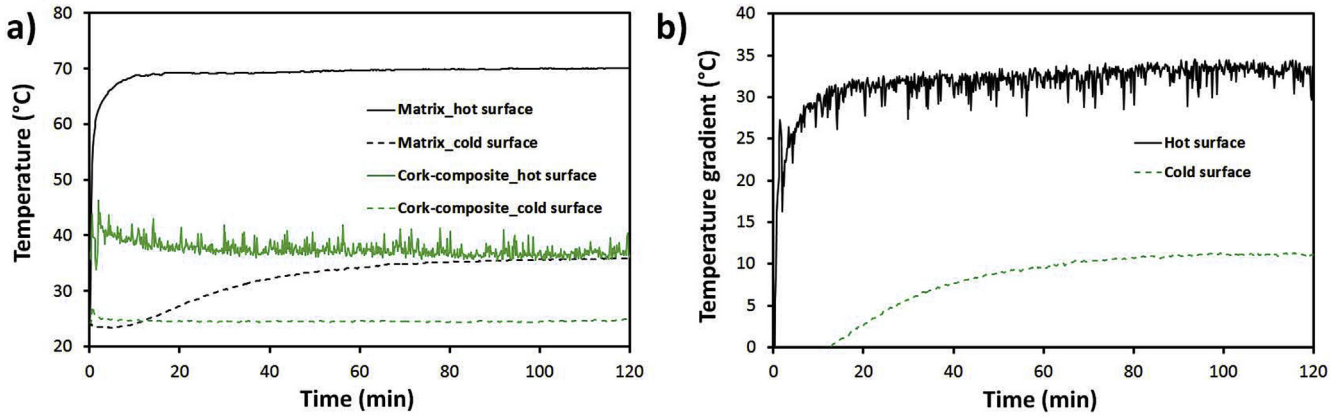

Fig. 9. (a) Temperature fluctuation of the *hot* and cold *surface* of the matrix and the highest cork-containing composite (92 vol.% cork), when a temperature gradient between the surfaces is imposed; while b) represents the difference in temperature between the matrix and the composite surfaces.

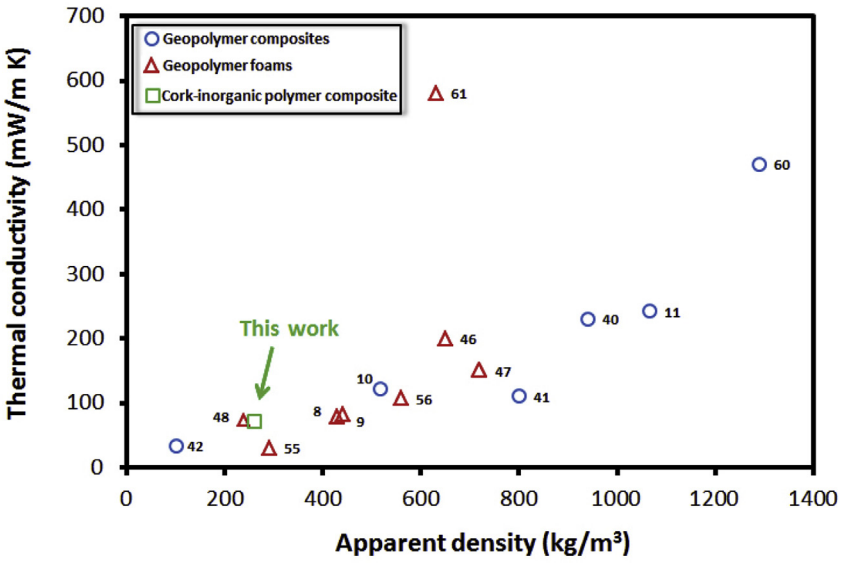

Fig. 10. Thermal conductivity of various inorganic polymer composites (blue circles) and foams (red triangles) reported in literature. The lowest thermal conductivity value here achieved was also included (green square). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

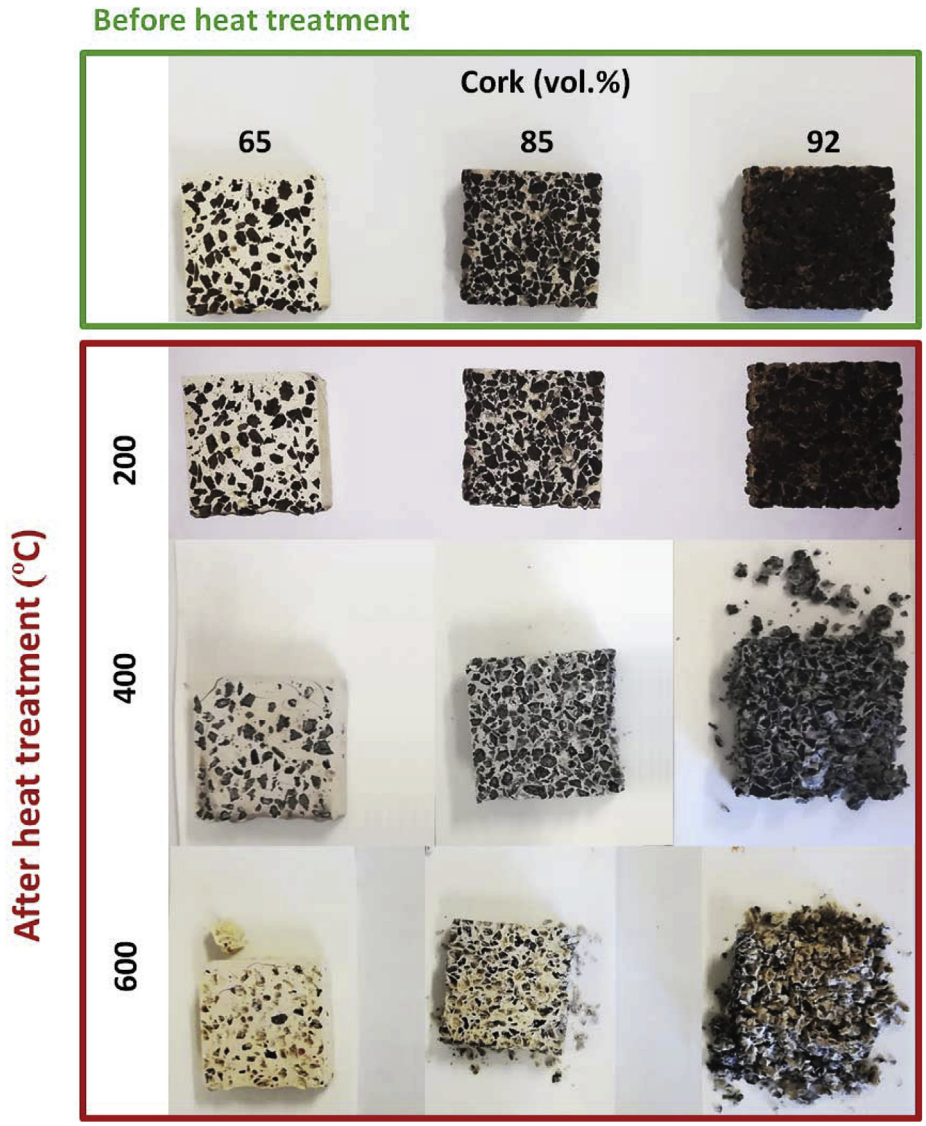

Fig. 11. Digital pictures of the cork-inorganic polymer composites before and after thermal treatment illustrating the macrostructural changes promoted by the various firing temperatures.

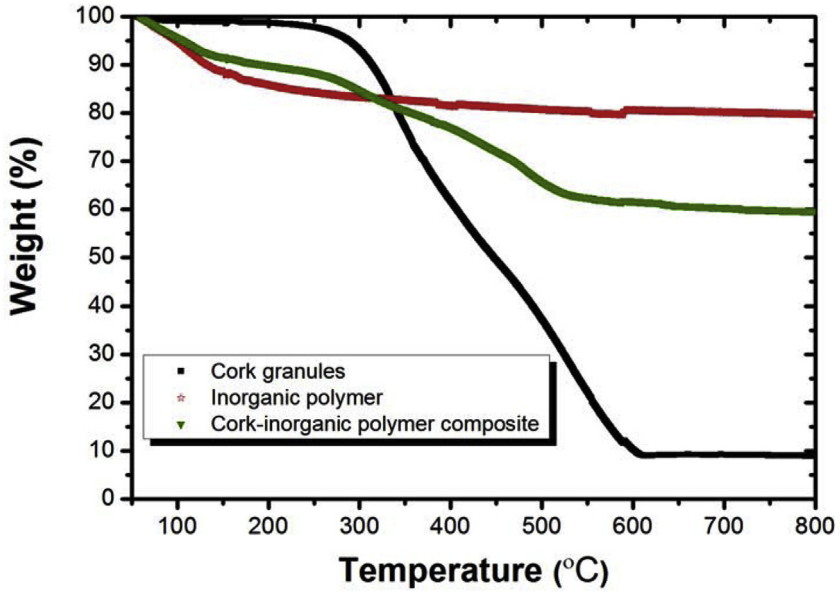

Fig. 12. TG curves of the black expanded cork granules, the inorganic polymer matrix and the cork-inorganic polymer composite prepared with 92 vol.% cork.

durability of the produced cork-inorganic polymer composites.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cemconcomp.2018.12.024.

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